Studies on the Mechanism of Friedel-Crafts Type Reactions. (VIII) : Alkylation of Benzene by Organic Esters

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coals with natural coals by softening swelling curve, owing to the difference of physical conditions.

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26. Studies on the Mechanism of Friedel-Crafts Type Reactions. (VIII)

Alkylation of Benzene by Organic Esters

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Esters of carboxylic acids can alkylate benzene in the presence of more than 1 mol aluminium halide per mol esters at the temperature below 50°C without accompanying acylation. (Bowden: J. Am. Chem. Soc. **60** 645 (1938)) Norris (J. Am. Chem. Soc. **62** 874 (1940)) obtained ethyl chloride and $CH_3COOAlCl_2$ when equimolecular amount of ethyl acetate and $AlCl_3$ was heated at 140–170°C and suggested the mechahism that the alkylation by the ester proceeds through an intermediate formation of alkyl halide (RCl). According to this mechanism the rate of formation of RCl and that of alkylation by the ester must be in the same order of magnitude, because the rate of alkylation of benzene by RCl is very large.

The authors studied the reactions between ethylacetate and $AlBr_3$ at 20°C (at this temperature ethylation of benzene proceeds smoothly). Only 4–9 % of ethylacetate was decomposed even in the presence of excess $AlBr_3$ without any formation of ethyl bromide. Kinetical studies showed that the rate of alkylation is first order in esters and its rate constant is proportional to the concentration of free $AlBr_3$ (i. e. total $AlBr_3$ concentration minus ester concentration). These result may be explained by the following mechanism: (1) only free $AlBr_3$ has catalytic activity and the $AlBr_3$ combined with the ester (1 : 1 mol complex) is catalyticaly inactive, (2) probably alkyl cation, accepted active intermediate of Friedel-Crafts reactions, may be formed by the interaction of free $AlBr_3$ and ester-$AlBr_3$ complex, (3) the alkyl cation alkylates benzene and never produces alkyl halide.

The velocity of alkylation is affected by structural change of R in the esters (R'COOR) in the order: ethyl acetate 0.41 <n-propyl acetate 0.82 <n-butyl acetate 0.85 (min^{-1} per mol/l $AlBr_3$). This order of reaction rate agrees with that of RCl and indicates that the inductive effect of alkyl group facilitate the attack of $AlBr_3$ on the oxygen atom of alkoxy group. The order of reaction rate caused by the structural change of R' is as follows: ethyl formate 2.07 >ethyl acetate 0.41> ethyl butyrate 0.084, which shows that the strengh of O–R bond is increased by the inductive effect of alkyl group in the acid residue.
